Heteroatom Chemistry
Volume 12, Number 5, 2001

Dynamic Behavior of Pentacoordinate Organogermanium Carboxylic Acids and Their Pyridinium Salts

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Received 3 February 2001; revised 01 April 2001

ABSTRACT: *Solution structures of some pentavalent organogermanium compounds have been investigated. Variable temperature NMR studies of these compounds revealed that concomitant Berry pseudorotation and prototropy occur, which make the two protons of the CH_2 moiety nonequivalent at lower temperatures.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:451–456, 2001

INTRODUCTION

In a previous communication [1], we reported that 2-(2-*t*-butyl-5-oxo-1,3,2-oxathiagermolan-2-ylthio)acetic acid (**1**) adopted, in the crystal structure, the chiral trigonal bipyramidal structure (**1a**) (see Figure 1) with an equatorial *t*-butyl group and two equatorial Ge–S bonds. There are two apical Ge–O bonds; one is a covalent Ge–O bond of the germathialactone moiety, and the other is a Ge–O bond between the carbonyl oxygen of the $-SCH_2COOH$ moiety coordinated to the germanium atom. The orientation of the substituents is in line with the Muetterties rule [2]. Another interesting structural feature of **1a** is the intermolecular hydrogen bonding in the crystal structure in which the hydrogen atom of the carboxy group is hydrogen bonded to the germathialactone carbonyl oxygen of an adjacent molecule. There remains, however, one interesting problem, namely, the structure of **1** in solution. One possibly is that **1** also has a pentacoordinate structure **1a** in solution. The second possibility is that **1** has a tetravalent state (**1b**) (see Figure 1) with a free $-SCH_2COOH$ side chain. The existence of a carboxy group in the solid state is evidenced by an absorption

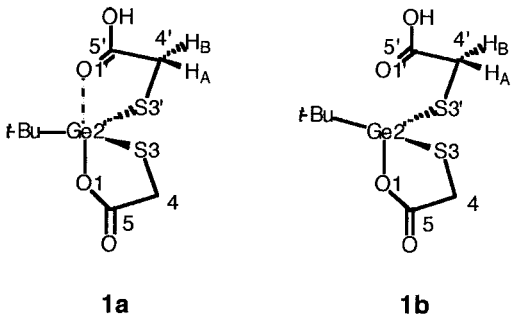

FIGURE 1 Structures of **1a** and **1b**.

Dedicated to Prof. Naoki Inamoto on the occasion of his 72nd birthday.

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Contract Grant: Ministry of Education, Science, Sports, Culture, and Technology.
Contract Grant Number: Grant-in-Aid for Scientific Research 11640547.

at 3447 cm^{-1} in the IR spectrum of **1**. In this article, we intend to describe our NMR study on the solution structure of **1** and related compounds.

RESULTS AND DISCUSSION

Whatever may be the solution structure of **1**, we initially expected that two signals should be observed in the methylene region: one for the germathialactone moiety (H4), and the other for the $-SCH_2COOH$ moiety (H4′) in the ^1H NMR spectra, and similarly, two signals each should be observed in the methylene (C4 and C4′) region and the carbonyl region (C5 and C5′) of the ^{13}C NMR spectrum because the chemical shift differences for these two moieties can be large [3]. The ^1H NMR spectrum of **1** exhibited, however, only one signal at δ 3.86 for H4 and H4′, as is shown in Figure 2.

It must be added that a broad OH signal (of the carboxy group) is observed at δ 11.10 in the ^1H NMR spectra of **1**. The ^{13}C NMR spectrum also gave only one peak at δ 31.91 for C4 and C4′ and one peak at δ 176.06 for C5 and C5′, respectively, at ambient temperature in acetone-d_6. These results indicate that a process occurs that makes the germathialactone and $-SCH_2COOH$ side chain equivalent in the NMR timescale. To elucidate the nature of this rate process, a variable temperature study was attempted for **1**. The ^1H NMR spectrum of the methylene signals for **1** showed a temperature-dependent phenomenon; the singlet observed at ambient temperature split into an AB quartet with decreasing probe temperature, as indicated in Figure 3.

The free energy of activation as estimated by the DNMR3 [4] analysis (summarized in Table 1) is 12.3 kcal mol^{-1}. Further cooling to *ca.* 180 K did not, however, cause any additional splitting or significant broadening. Thus, in the ^{13}C NMR spectra, the resonance for the C=O region remained as a singlet even at 180 K. As for the origin of these temperature effects on the NMR spectra, the freezing of the inversion of the five-membered rings at low temperature could be one explanation. However, the barrier for such a process should be much lower than the observed values. Furthermore, this process alone could not explain the observed equivalence of carbon signals at lower temperatures. Another possibility is that the Ge–O bond cleavage and reformation as applied to the trigonal bipyramidal structure in a manner analogous to an S_N2 type of an unstable intermediate. However this process could not explain the nonequivalence of the methylene protons. Also a concomitant nonequivalence, for instance, of the two carbonyl carbons C5 and C5′ is not likely for the reason discussed previously. We believe that the process actually involved is a Berry pseudorotation [5,6] or a turnstile rotation [6]. Several successive pseudorotations can convert **1** to its enantiomer, in which H_A and H_B in **1** exchange their positions. This can explain the rate process observed for the methylene protons, but the equivalence of, for instance, the two

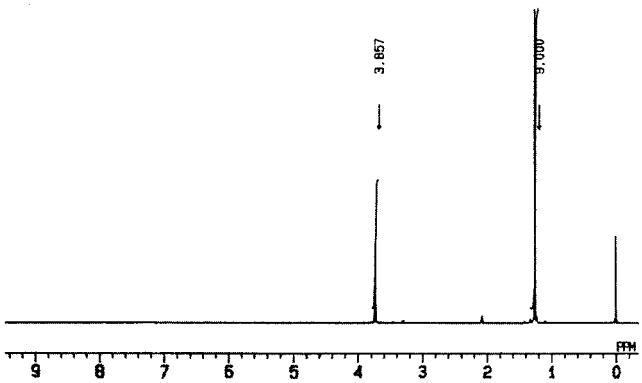


FIGURE 2 ^1H NMR spectra of **1** (in acetone-d_6).

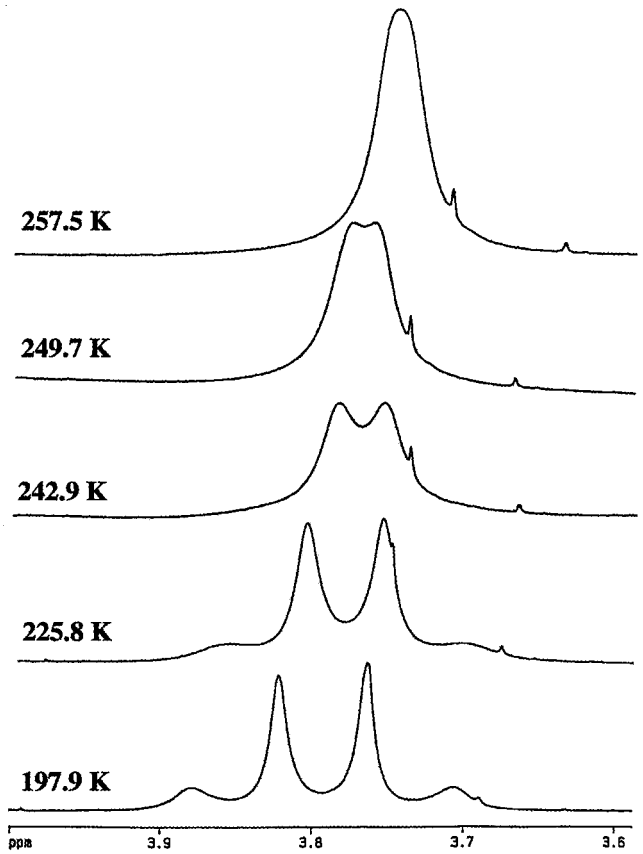


FIGURE 3 Variable temperature ^1H NMR spectra of **1** (CH_2 portion).

carbonyl carbons (C5 and C5′) cannot be explained by this process alone. Thus, we suggest that, in addition to this rotation, a rapid prototropy from the upper part of the molecule to the lower part (and *vice versa*) takes place, which makes the two parts of the molecule averaged (Scheme 1).

The calculated barrier for the pseudorotation of a simple system such as PH_5 is as low as 1.9 kcal mol^{-1} [7]. In such a simple trigonal bipyramid such as PF_5, the freezing of exchange between apical and equatorial F atoms is not observed even at 93 K. For compound **1**, at least one oxygen atom should occupy one of the equatorial position if pseudorotation is to take place, which is contrary to Muetterties rule [2] and is thus unfavorable. This is why the pseudorotation barrier for cyclic species such as **1** or **2** can be higher since the value will depend on the pathway (i.e., the transition state) [8]. Since it is likely that the prototropy barrier is very low, the additional influence of this effect can support our observation that only one rate process occurs in the range of the NMR timescale. Although Berry pseudorotation and turnstile rotation are well documented for hypervalent silicon compounds [8], to the best of our knowledge, this is the first report on pseudorotation for hypercoordinated organogermanium compounds.

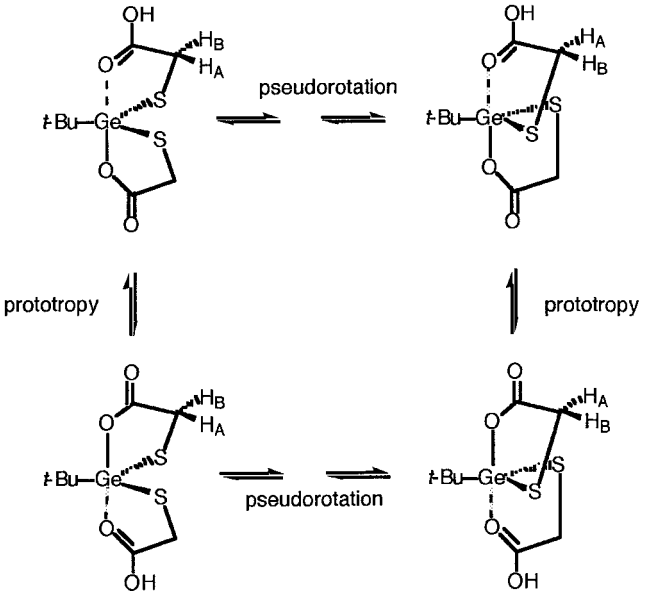
We further wished to determine if the bulky *t*-Bu group bonded to the germanium atom facilitates this rate process. Another factor that may facilitate the rate process is the presence of a coordinated carboxy group or the prototropy. To answer these questions, we prepared 2-(2-phenyl-5-oxo-1,3,2-oxathiagermolan-2-ylthio)acetic acid (**2**), which has a less bulky group on the germanium, and the pyridinium salts **3** and **4**. The pyridinium salts were chosen because these salts are soluble in some organic solvents so that NMR study is possible. In addition, both **3** and **4** gave good crystals suitable for X-ray crystallographic analysis. Our preliminary X-ray analysis of compounds **2–4** indicated that all these compounds have the trigonal bipyramida1 structure in the crystal state, as shown in Figure 4.

Variable temperature ^{1}H NMR study of **2–4** also exhibited a rate process for methylene protons but no additional change upon further cooling. The splitting pattern of **2–4** are shown in Figures 5–7, and the estimated free energy of activation together with other relevant data for **1–4** are listed in Table 1. Resemblance of the structures among **1–4** is obvious.

Thus, the structural requirement for the observed rate process is solely the presence of one $-SCH_2COOH$ (or $-SCH_2COO^-$) moiety and one germathialactone ring, and neither the size of the hydrocarbon substituent on the germanium nor the formation of hydrogen bonding contribute much to the rate process and hence the pentacoordination. A study to determine the solid state structures of **2–4** is in progress in our laboratory.

EXPERIMENTAL

Solvents were dried and purified in a conventional manner. All the reactions were carried out under nitrogen. Silica-gel column chromatography was performed on silica gel 7734 (Merck, 70-230 mesh). Melting points were determined on a Yanaco MP-S melting point apparatus and are uncorrected. The NMR experiments were carried out on a JEOL EX 400 FT-NMR SYSTEM (400 MHz) or Bruker ARX-300 (300 MHz) spectrometer. Sample concentrations were 17 mg/mL of solvents with use of a 5 mm (o.d.)



SCHEME 1 The rate processes in **1**.

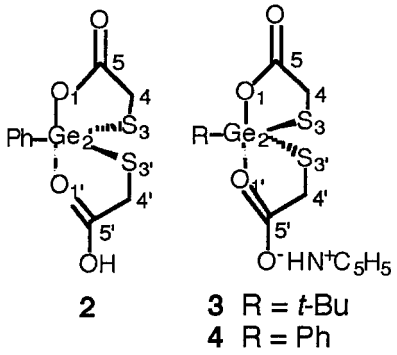


FIGURE 4

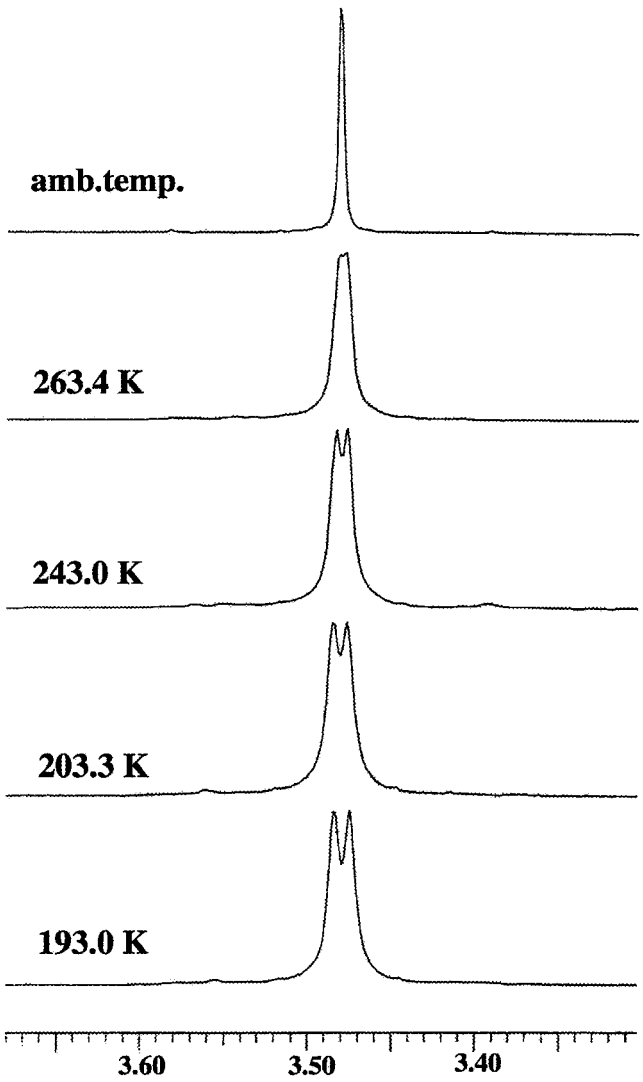


FIGURE 5 Variable temperature ^{1}H NMR spectra of **2** (CH_2 portion).

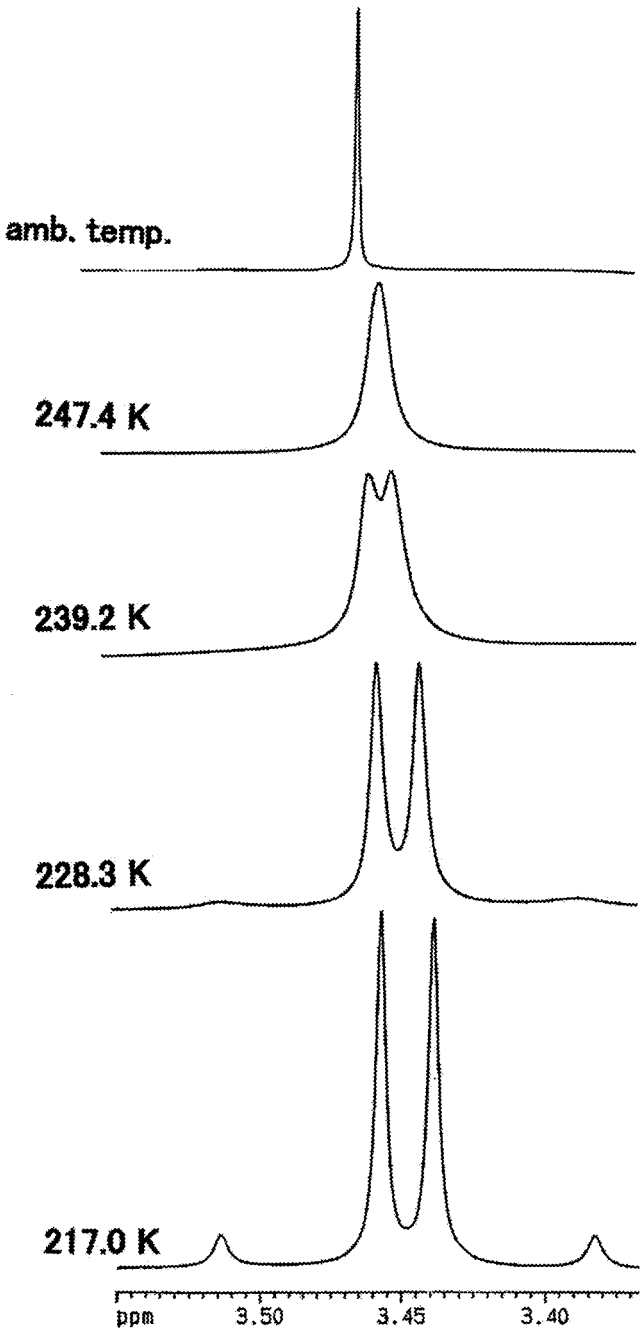


FIGURE 6 Variable temperature ^{1}H NMR spectra of **3** (CH_2 portion).

sample tube with tetramethylsilane (TMS) as the internal standard. For variable temperature studies, the characteristic solvent peaks were used as internal references. The temperature of the sample was calibrated by means of a standard sample of neat methanol whose internal chemical shift was accurately measured as a function of temperature. The IR specta were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrophotometer. Elemental analyses were performed by the Elemental Analysis Laboratory, Department of Chemistry, Graduate School of Science, the University of Tokyo. Line-shape analysis was carried out by using the spin-simulation program DNMR3K, a modified version of DNMR3 [3], in the case of a 2-nuclei-2-chemical configuration system. The spin-spin relaxation time (T_2) was estimated from the line-width measurements evaluated at half height of the spectrum. Chemical shift differences were read at several temperatures at slow exchange regions, and these values were extrapolated to the temperature where line-shape analysis was performed.

*Preparation of 2-(2-t-Butyl-5-oxo-1,3,2-oxathiagermolan-2-ylthio)acetic Acid (**1**)*

To a mixture of mercaptoacetic acid (14.7 g, 159.7 mmol) and pyridine (27.3 g) in benzene (100 mL), *t*-

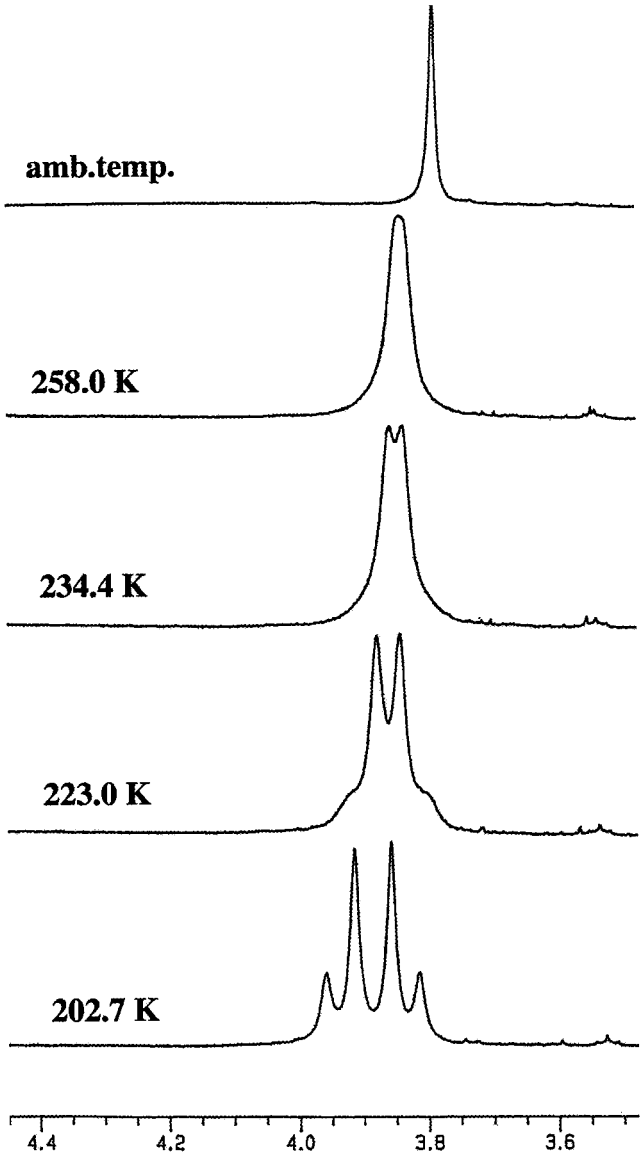


FIGURE 7 Variable temperature ^{1}H NMR spectra of **4** (CH_2 portion).

TABLE 1 Barriers to Exchange of Methylene Protons

Solvent	δ/ppm	T_c/K	$\Delta\delta$/Hz	J_{AB}	k/sec^{-1}	$\Delta G^{\neq}$ (kcal mol^{-1})
1 acetone-d_6	3.76	249.7	24.6	17.8	69.0	12.2
2 acetone-d_6	3.47	248.0	10.5	19.9	52.5	12.4
3 CD_2Cl_2:CS_2 = 2:1 (v/v)	3.47	239.2	14.7	17.4	43.0	12.1
4 CD_2Cl_2	3.80	234.4	14.7	17.0	75.0	11.6

δ, chemical shifts of the peaks monitored; T_c, coalescent temperature; $\Delta\delta$, chemical shift difference in Hz when the exchange is frozen; k, rate constant of exchange; $\Delta G^{\neq}$, free energy of activation.

butyltrichlorogermane [9] (12.50 g, 52.9 mmol) in tetrahydrofuran (THF) (100 mL) was added at room temperature under nitrogen, and the mixture was stirred for 15 hours. The mixture was neutralized with *aq* HCl (1 mol dm^{-3}), and the organic layer was separated, washed with water, and dried over Na_2SO_4. The solvent was removed to obtain the crude product, and the residual solid was recrystallized from a mixture of ethyl acetate and ethanol to give colorless crystals of **1** (3.40 g, 20%): m.p. 154°C. IR (KBr); 3447 (OH), 1617 (C=O) cm^{-1}. ^{1}H NMR (acetone-d_6, 300 MHz); δ 11.0 (b, OH, 1H), 3.73 (s, CH_2, 4H), 1.23 (s, *t*-Bu, 9H), ^{13}C NMR (acetone-d_6, 100 MHz); δ 176.1 (s, C=O), 39.3 (s, $\underline{C}(CH_3)_3$), 31.9 (t, SCH_2), 27.9 (q, CH_3). Anal. Calcd for $C_8H_{14}O_4S_2Ge$: C, 30.91; H, 4.54. Found: C, 30.79; H, 4.57%.

*Preparation of 2-(2-Phenyl-5-oxo-1,3,2-oxathiagermolan-2-ylthio)acetic Acid (**2**)*

To a mixture of mercaptoacetic acid (10.8 g, 117 mmol) and pyridine (18.8 g) in benzene (100 mL), phenyltrichlorogermane [9] (10.0 g, 39 mmol) in THF (50 mL) was added at room temperature, and the mixture was stirred for 24 hours. The mixture was neutralized with *aq* HCl (1 mol dm^{-3}), and additional THF (50 ml) was added. The organic layer was separated, washed with water, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residual solid (5.1 g) was dissolved in benzene. The insoluble fraction was filtered off and dried *in vacuo* to afford colorless crystals of **2**, (1.93 g, 16%): m.p. 226–228°C. IR (KBr); 3445 (OH), 1629 (C=O), 1629 (C=O) cm^{-1}. ^{1}H NMR (acetone-d_6, 400 MHz); δ 7.74–7.44 (m, Ph, 5H), 3.82 (s, CH_2, 4H). ^{13}C NMR (acetone-d_6, 100 MHz); δ 176.3 (s, C=O), 140.0, 133.0, 131.6, 129.6, 32.0 (t, SCH_2). Anal. Calcd for $C_{10}H_{10}O_4S_2Ge$: C, 36.24; H, 3.04, S 19.37. Found: C, 36.50; H, 3.17, S 19.44%.

*Preparation of Pyridinium 2-2-t-butyl-5-oxo-1,3,2-oxathiagermolan-2-ylthio)acetate (**3**)*

Compound **1** (1.0 g, 3.24 mmol) was dissolved in THF (50 mL), and pyridine (0.60 g, 7.50 mmol) was added dropwise at room temperature. Colorless needles precipitated immediately. After 1 hour, the crystals were collected, washed with THF and Et_2O, and recrystallized from THF/diethyl ether to give colorless needles of **3**, m.p. 155–157°C (0.87 g, 69%). IR (KBr) 1667 (C=O) cm^{-1}. ^{1}H NMR (CD_2Cl_2/CS_2, 400 MHz); δ 8.81–8.02 (m, arom, 5H), 3.47 (s, CH_2, 4H). ^{13}C NMR (CD_2Cl_2/CS_2, 100 MHz); δ 175.8 (s, C=O), 145.7, 141.3, 127.2, 36.9 (s, $\underline{C}(CH_3)_3$), 32.0 (t, SCH_2), 27.3 (q, CH_3). Anal. Calcd for $C_{13}H_{19}NO_4S_2Ge$: C,

40.03; H, 4.91, N 3.59, S 16.44. Found: C, 39.98; H, 4.68 N 3.60, S 16.64%.

*Preparation of Pyridinium 2-(2-Phenyl-5-oxo-1,3,2-oxathiagermolan-2-ylthio)acetate (**4**)*

Compound **2** (0.5 g, 1.2 mmol) was dissolved in THF (20 mL), and pyridine (0.12 g, 1.50 mmol) was added dropwise at room temperature. Colorless needles precipitated immediately. After 1 hour, the crystals were collected, washed with THF and Et_2O, and recrystallized from acetonitrile/ethyl acetate to give colorless needles of **4**: m.p. 188–190°C (0.23 g, 47%). IR (KBr) 1671 cm^{-1} (C=O). ^1H NMR (CD_2Cl_2), 400 MHz); δ 8.66–8.35 (m, arom, 5H), 7.91–7.37 (m. Ph, 5H), 3.56 (s, CH_2, 4H). ^{13}C NMR (CD_2Cl_2, 100 MHz); δ 175.4 (s, C=O), 145.6, 142.6, 132.4, 130.0, 32.3 (t, SCH_2). Anal. Calcd for $C_{15}H_{15}NO_4S_2Ge$: C, 43.94; H, 3.68, N 3.41, S 15.64. Found: C, 43.87; H, 3.67, N 3.41, S 15.36%.

ACKNOWLEDGMENTS

We thank Dr. M. Minoura, Kitasato University, for variable discussion.

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